

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 308 496 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

07.05.2003 Bulletin 2003/19

(21) Application number: **02257642.5**

(22) Date of filing: **05.11.2002**

(51) Int Cl.7: **C10M 141/10, C10M 167/00**

// (C10M141/10, 133:44,
135:36, 137:02),
(C10M167/00, 125:24, 133:44,
133:52, 133:56, 135:36, 137:02,
137:10, 145:14, 159:16,
159:24), C10N30:06,
C10N40:04

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR
Designated Extension States:
AL LT LV MK RO SI**

(30) Priority: **06.11.2001 US 332932**

(71) Applicant: **The Lubrizol Corporation
(an Ohio corporation)
Wickliffe Ohio 44092-2298 (US)**

(72) Inventors:

- **Sumiejski, J.L.
Mentor, Ohio 44060 (US)**
- **Ward, William C.Jr.
Perry, Ohio 44081 (US)**

(74) Representative: **Crisp, David Norman et al
D. YOUNG & CO.
21 New Fetter Lane
London EC4A 1DA (GB)**

(54) **Transmission fluids exhibiting reduced pitting**

(57) Compounds comprising a 5-membered ring containing at least two double bonded nitrogen atoms can be used to impart improved metal pitting performance to a transmission fluid. The fluid includes an oil of lubricating viscosity and a hydrocarbyl ester of a phos-

phorous acid and is preferably limited to 0 to 0.1 percent by weight of zinc salts of sulfur-containing phosphorus acids.

EP 1 308 496 A2

Description**BACKGROUND OF THE INVENTION**

5 [0001] The present invention relates to the use of a compound to reduce metal pitting performance in a transmission fluid.

[0002] There are many types of transmissions which are used in vehicle applications. Common well known types of transmissions include manual transmissions, perhaps the oldest type, and various types of automatic transmissions. Manual transmissions and certain manual transmission fluids solving certain of the problems associated with manual transmissions are disclosed in U.S. Patent 4,792,410 Schwind et al., December 20, 1988. Automatic transmissions of the conventional variety and certain automatic transmission fluids solving certain of the problems associated with automatic transmissions are disclosed in European Patent Publication 987,311, March 33, 2000, discussed below, and in U.S. patent 5,858,929, Sumiejski et al., January 12, 1999.

15 [0003] Continuously variable transmissions (CVTs) represent generally a more recent development. A description of CVTs, including a popular variety, the push-belt CVT, and fluids suitable for use therein is found in U.S. Patent 5,750,477, Sumiejski et al., May 12, 1998. Another device which may fall within the description of a CVT is a traction drive. Traction drives are devices in which power or torque is transmitted from an input element to an output element through nominal point or line contact, typically with a rolling action, by virtue of the traction between the contacting elements. Traction drives can be generally used in automotive or industrial machinery for transmitting power between rotating members. Traction fluids and traction drives in which they can be used have been described for instance, in U.S. Patents 4,693,134 and 5,043,497.

[0004] There are also hybrid transmissions of various types including dual clutch transmissions which have been developed by Borg Warner and are described, for instance, in U.S. Patent 5,385,064, Reece, January 31, 1995.

25 [0005] Various types of transmission fluids have been proposed for all types of transmissions, including especially for continuously variable transmissions.

[0006] PCT Publication WO0070001, November 23, 2000, discloses high boron formulations for continuously variable transmissions. Among the disclosed components are metal deactivators such as tolyltriazole, benzotriazole, and the methylene-coupled product of tolyltriazole and amines such as 2-ethylhexylamine. Such metal deactivators can be useful in adjusting the metal-to-metal friction in push belt CVTs.

30 [0007] European Patent Application 781 805, March 12, 1997 discloses lubrication fluids for reduced air entrainment, using 2,5-dimercapto-1,3,4-thiadiazole to provide antiwear properties, along with certain antifoam agents. The fluids can be continuously variable transmission fluids. The oil has a kinematic viscosity of 2-10 cSt at 100°C and the composition has a Brookfield viscosity of less than 20,000 cP at -40°C.

[0008] European Patent Application 987 311, March 22, 2000 discloses transmission fluid compositions, especially for continuously variable transmissions. Corrosion inhibitors can be included in the composition.

35 [0009] All such transmissions are subject to pitting if the fluid used therein does not provide adequate protection. The present invention solves the problem of pitting of metal surfaces in transmissions, especially continuously variable automatic transmissions, by including in the transmission fluid an effective amount of one or more selected compounds which are typically known for use as metal deactivators. The presence of these materials also serves to provide improved (increased) metal-on-metal friction values. These materials are particularly useful in fluids which contain very low amounts of zinc salts of sulfur-containing phosphorus acids.

SUMMARY OF THE INVENTION

45 [0010] The present invention provides for the use of at least one compound comprising a 5-membered ring containing at least two double bonded nitrogen atoms, to impart improved metal pitting performance to a fluid when said fluid is used in the lubrication of a continuously variable automatic transmission;

50 wherein said fluid comprises an oil of lubricating viscosity, and wherein said fluid further comprises a hydrocarbyl ester of a phosphorus acid. The fluid preferably contains 0 to 0.1 percent by weight of zinc salts of sulfur-containing phosphorus acids.

DETAILED DESCRIPTION OF THE INVENTION

[0011] Various preferred features and embodiments will be described below by way of non-limiting illustration.

55 [0012] The first component of the present invention is an oil of lubricating viscosity which is generally present in a major amount (i.e. an amount greater than 50% by weight). Generally, the oil of lubricating viscosity is present in an amount of greater than 80% by weight of the composition, typically at least 85%, preferably 90 to 95%. Such oil can be derived from a variety of sources, and includes natural and synthetic lubricating oils and mixtures thereof.

[0013] The natural oils useful in making the inventive lubricants and functional fluids include animal oils and vegetable oils (e.g., lard oil, castor oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic/naphthenic types which may be further refined by hydrocracking and hydrofinishing processes and are dewaxed. Oils of lubricating viscosity derived from coal or shale are also useful. Useful natural base oils may be those designated by the American Petroleum Institute (API) as Group I, II, or III oils. Group I oils contain < 90% saturates and/or > 0.03% sulfur and have a viscosity index (VI) of ≥ 80 . Group II oils contain $\geq 90\%$ saturates, $\leq 0.03\%$ sulfur, and have a VI ≥ 80 . Group III oils are similar to group II but have a VI ≥ 120 .

[0014] Upon occasion, highly refined or hydrocracked natural oils have been referred to as "synthetic" oils. More commonly, however, synthetic lubricating oils are understood to include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like. Polyalpha olefin oils are also referred to as API Group IV oils.

[0015] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified such as by esterification or etherification constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, or diethyl ether of polypropylene glycol having a molecular weight of 1000-1500) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_{3-8} fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol.

[0016] Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, or alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, or propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diloctyl azelate, dilsodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0017] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, or tripentaerythritol.

[0018] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-hexyl)silicate, tetra-(p-tert-butylphenyl) silicate, hexyl-(4-methyl-2-pentoxyl)disiloxane, poly(methyl) siloxanes, poly-(methylphenyl)siloxanes). Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid), polymeric tetrahydrofurans and the like.

[0019] Another class of oils is known as traction oils, which are typically synthetic fluids containing a large fraction of highly branched or cycloaliphatic structures, i.e., cyclohexyl rings. Traction oils or traction fluids are described in detail, for example, in U.S. Patents 3,411,369 and 4,704,490.

[0020] Unrefined, refined, and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, hydroprocessing, hydrocracking, and hydrotreating. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0021] In one embodiment, the oil of lubricating viscosity is a poly-alpha-olefin (PAO). Typically, the poly-alpha-olefins are derived from monomers having from 4 to 30, or from 4 to 20, or from 6 to 16 carbon atoms. Examples of useful PAOs include those derived from 1-decene. These PAOs may have a viscosity from 2 to 150 cSt.

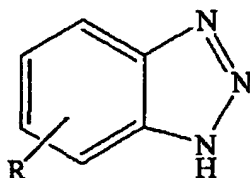
[0022] The present invention can be used in transmission fluids which contain only a limited amount of zinc salts of sulfur-containing phosphorus acids. The limited amount is typically 0 to 0.1 percent by weight, more preferably up to

0.05 percent by weight. In another embodiment, the fluid is substantially free from such salts, that is, less than 0.01 percent by weight. Typical examples of zinc salts of sulfur-containing phosphorus acids are the zinc dialkyl dithiophosphates. Such salts are well known to those skilled in the art of lubricant formulation. They are typically used to impart extreme pressure performance to various lubricating compositions. They are well known to those in the art of lubricant additives. They and their method of preparation are described, for instance in U.S. patent 4,981,602 (component (C), columns 29-35). While zinc dialkyl dithiophosphates can be also be used to impart high metal-to-metal friction to compositions for continuously variable transmissions, their use in automatic transmission fluids is problematic because of their low thermal and oxidative stability and occasional problems with clutch compatibility.

[0023] To the transmission fluid of the present invention is included one or more compounds which are conventionally used as metal deactivators, for the purpose of imparting improved anti-pitting performance. Metal deactivators are typically nitrogen and/or sulfur containing heterocyclic compounds, such as triazoles, amino-mercaptothiadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines, and derivatives of any one or more thereof. For the present invention, the materials of interest are typically characterized by the presence in their structure of a 5-membered ring containing at least two double bonded nitrogen atoms. Such molecules may be also characterized by sp^2 hybridization of orbitals within the ring, and a measure of electron delocalization and non-benzene aromatic character within the ring.

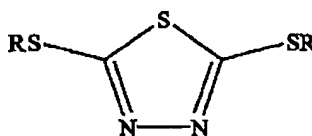
[0024] The materials of this additive component used in this invention are typically one or more compounds selected from the group consisting of aromatic triazoles and mercaptothiadiazoles. In one embodiment, the fluid comprises both an aromatic triazole and a mercaptothiadiazole.

[0025] Aromatic triazoles are materials having the general structure



shown here as a substituted benzotriazole. Analogous aromatic materials are also included, which can be based on naphthalene and other aromatic structures. In the above structure, R is hydrogen or a hydrocarbyl group, typically of 1 to 8 carbons, preferably 1 or 2 carbons. When R is methyl, the material is tolyltriazole.

[0026] Mercaptothiadiazoles are materials generally having the general structure



In the structure shown, each R is hydrogen or a hydrocarbyl group having 1 to 30 carbon atoms, preferably, 6 to 15 carbons atoms. R can also represent a sulfur-containing group, R'S-, so that there can be a chain of two sulfur atoms linking the thiadiazole nucleus to the hydrocarbyl group. Such materials are, for instance, dihydrocarbyldithiothiadiazoles.

[0027] A preferred aromatic triazole is tolyl triazole. Other suitable aromatic triazoles include benzotriazole.

[0028] A preferred mercaptothiadiazole is 2,5-bis-(tert-nonyldithio)-1,3,4-thiadiazole. Other mercaptothiadiazoles include various derivatives of 2,5-dimercaptothiadiazoles ("DMTD"), including (a) 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazole or 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazole and mixtures thereof; (b) carboxylic esters of DMTD; (c) condensation products of α -halogenated aliphatic monocarboxylic acids with DMTD; (d) reaction products of unsaturated cyclic hydrocarbons and unsaturated ketones with DMTD; (e) reaction products of an aldehyde and diaryl amine with DMTD; (f) amine salts of DMTD; (g) dithiocarbamate derivatives of DMTD; (h) reaction products of an aldehyde, and an alcohol or aromatic hydroxy compound, and DMTD; (i) reaction products of an aldehyde, a mercaptan, and DMTD; (j) 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazole; (k) products from combining an oil-soluble dispersant

with DMTD; and mixtures thereof. Compositions (a) - (k) are known to those skilled in the art and are described in U. S. Patent 4,612,129 and patent references cited therein. Among the preferred thiadiazoles for use in this invention are those listed in (a), (h), and (k) above.

[0029] The total amount of the one or more anti-pitting additives described above is generally 0.01 to 0.5 percent by weight of the finished composition. Preferred ranges include 0.03 to 0.1 percent by weight, which is especially preferred when other materials such hydrocarbyl esters of phosphorus acids (described below) are present.

[0030] Other conventional components may be present in the transmission fluid. One particularly desirable class of materials are those known as dispersants, and in particular, acylated amine dispersants such as succinimide dispersants.

[0031] Acylated amine dispersants include reaction products of one or more carboxylic acylating agent and one or more amine. The carboxylic acylating agents include C_{8-30} fatty acids, C_{14-20} isoaliphatic acids, C_{18-44} dimer acids, addition dicarboxylic acids, trimer acids, addition tricarboxylic acids, and hydrocarbyl substituted carboxylic acylating agents. Dimer acids are described in U.S. Pat. Nos. 2,482,760, 2,482,761, 2,731,481, 2,793,219, 2,964,545, 2,978,468, 3,157,681, and 3,256,304. The addition carboxylic acylating agents are addition (4+2 and 2+2) products of an unsaturated fatty acid with one or more unsaturated carboxylic reagents, which are described above. These acids are taught in U.S. Pat. No. 2,444,328. In one embodiment, the carboxylic acylating agent is a hydrocarbyl substituted carboxylic acylating agent. The hydrocarbyl substituted carboxylic acylating agents are prepared by a reaction of one or more of the above olefins or polyalkenes with one or more of the above unsaturated carboxylic reagents, such as maleic anhydride. The amines can be any of those described elsewhere herein, preferably a polyamine, such as an alkylene-polyamine or a condensed polyamine. Acylated amines, their intermediates and methods for preparing the same are described in U.S. Pat. Nos. 3,219,666; 4,234,435; 4,952,328; 4,938,881; 4,957,649; 4,904,401; and 5,053,152. The preferred materials, succinimide dispersants, are prepared by the reaction of an amine and a hydrocarbyl substituted succinic anhydride or the reactive equivalent thereof. These are very well known materials in the art of lubricant formulation and are described in detail in numerous patents, including U.S. Patents 3,172,892 and 4,234,435.

[0032] Other types of dispersants which may be used include carboxylic esters, Mannich reaction products, hydrocarbyl substituted amines. These materials and methods of their preparation are described in greater detail in PCT publication WO00/70001 and references cited therein.

[0033] The dispersant can also be a modified dispersant, for example, a borated dispersant. Typically, the borated dispersant contains from 0.1% to 5%, or from 0.5% to 4%, or from 0.7% to 3% by weight boron. In one embodiment, the borated dispersant is a borated acylated amine, such as a borated succinimide dispersant. Borated dispersants are described in U.S. Pat. Nos. 3,000,916; 3,087,936; 3,254,025; 3,282,955; 3,313,727; 3,491,025; 3,533,945; 3,666,662, 4,925,983 and 5,883,057. Borated dispersants are prepared by reaction of one or more dispersants with one or more boron compounds.

[0034] Suitable boron compounds for preparing borated dispersants include various forms of boric acid (including metaboric acid, HBO_2 , orthoboric acid, H_3BO_3 , and tetraboric acid, $H_2B_4O_7$), boric oxide, boron trioxide, and alkyl borates of the formula $(RO)_x B(OH)_y$, wherein x is 1 to 3 and y is 0 to 2, the sum of x and y being 3, and where R is an alkyl group containing 1 to 6 carbon atoms. In one embodiment, the boron compound is an alkali or mixed alkali metal and alkaline earth metal borate. These metal borates are generally a hydrated particulate metal borate which are known in the art. Alkali metal borates include mixed alkali and alkaline metal borates. These metal borates are available commercially. Representative patents disclosing suitable alkali and alkali metal and alkaline earth metal borates and their methods of manufacture include U.S. patents 3,997,454; 3,819,521; 3,853,772; 3,907,601; 3,997,454; and 4,089,790.

[0035] The amount of the dispersant in the compositions of the present invention is typically 0 to 5 percent by weight, more commonly 0.5 to 3.0 percent by weight, and preferably 1.5 to 2.5 percent by weight.

[0036] Another common component for transmission fluids is a phosphorus compound, and in the present invention, in particular, an effective amount of a hydrocarbyl ester of a phosphorus acid will be present. Most phosphorus compounds impart a measure of anti-wear performance to the composition. However, as stated above, the fluids of the present invention may have no or only a limited amount of zinc salts of sulfur-containing phosphorus acids.

[0037] The phosphorus compound can be a phosphorus acid or ester of the formula $(R^1X)(R^2X)P(X)_nX_mR^3$ or a salt thereof, where each X is independently an oxygen atom or a sulfur atom, n is 0 or 1, m is 0 or 1, m+n is 1 or 2, and R^1 , R^2 , and R^3 are hydrogen or hydrocarbyl groups. Preferably at least one of R^1 , R^2 , and R^3 is a hydrocarbyl group, and preferably at least one is hydrogen. This component thus includes phosphorous and phosphoric acids, thiophosphorous and thiophosphoric acids, phosphite esters, phosphate esters, and thiophosphite and thiophosphate esters. The esters can be mono-, di- or tri-hydrocarbyl esters.

[0038] It is preferred that at least two of the X atoms in the above structure are oxygen, so that the structure will be $(R^1O)(R^2O)P(X)_nX_mH$, and more preferably $(R^1O)(R^2O)P(X)_nX_mH$. This structure can correspond, for example, to phosphoric acid when R^1 , R^2 , and R^3 are hydrogen. Phosphoric acid exists as the acid itself, H_3PO_4 and other forms equivalent thereto such as pyrophosphoric acid and anhydrides of phosphoric acid, including 85% phosphoric acid

(aqueous), which is the commonly available commercial grade material and is a preferred material for inclusion in the present transmission fluids. The formula can also correspond to a mono- or dialkyl hydrogen phosphite (a phosphite ester) when one or both of R^1 and R^2 are alkyl, respectively and R^3 is hydrogen, or a trialkyl phosphite ester when each of R^1 , R^2 , and R^3 is alkyl; in each case where n is zero, m is 1, and the remaining X is O. The structure will correspond to phosphoric acid or a related material when n and m are each 1; for example, it can be a phosphate ester such as a mono-, di- or trialkyl monothio phosphate when one of the X atoms is sulfur and one, two, or three of R_6 , R_7 , and R_8 are alkyl, respectively.

[0039] Dihydrocarbyl- or dialkyl hydrogen phosphites are among the phosphorus containing additives which may be used in the transmission fluids of the present invention. A common and preferred example of a dialkyl hydrogen phosphite is di-n-butyl hydrogen phosphite. Dihydrocarbyl hydrogen phosphites can be prepared by techniques well known in the art, and many such phosphites are available commercially.

[0040] Other examples of phosphorus-containing materials are phosphites and phosphates such as dibutyl phosphite (also known as dibutyl hydrogen phosphite), diphenylphosphite, triphenylphosphite, tricresylphosphate and triphenylthiophosphate. Triphenylphosphite is a preferred material. These materials are likewise well known and commercially available.

[0041] A more extensive listing of possible phosphorus compounds and references for their preparation can be found in the aforementioned PCT publication WO00/70001.

[0042] The suitable amounts of these phosphorus materials can be readily determined. If the phosphorus material is phosphoric acid, a typical amount is 0.0085 to 0.17 percent by weight of the composition. If the phosphorus material is a hydrocarbyl ester of a phosphorous acid, it will be typically present in amount of 0.025 to 0.5 percent by weight, and preferably 0.005 to 0.25 percent by weight, such as about 0.2 percent. Alternatively expressed, the hydrocarbyl ester of a phosphorous acid can be present in an amount to contribute 0.003 to 0.08 percent by weight phosphorus to the formulated fluid.

[0043] The transmission fluids of the present invention can contain other conventional components in customary amounts. Other such components include friction modifiers such as metal salts of fatty acids, fatty phosphites, fatty acid amides, fatty epoxides and borated derivatives thereof, fatty amines, glycerol esters and their borated derivatives, alkoxylated fatty amines (including ethoxylated fatty amines such as diethoxylated tallowamine) and their borated derivatives, isostearic acid condensation products of polyamines such as tetraethylene pentamine, such condensates containing amide and imidazoline or imine functional groups, alkyl-substituted imidazolines, sulfurized olefins, sulfurized polyolefins, sulfurized fats, and sulfurized fatty acids. They can also be suspended molybdenum disulfide, dialkyl or diaryl dithiophosphate molybdates or alkyl or dialkyl dithiocarbamate molybdates where the molybdenum is oxydisulfidobridged and chelated with dithiophosphate or dithiocarbamate ligands. Other conventional components include detergents such as overbased metal salts; viscosity modifiers, including hydrocarbon viscosity modifiers such as polybutenes, poly(ethylene/propylene) copolymers, and polymers of styrene with butadiene or isoprene, ester viscosity modifiers such as esters of styrene/maleic anhydride polymers, esters of styrene/maleic anhydride/acrylate terpolymers, and polymethacrylates, and dispersant viscosity modifiers; antioxidants, including hindered phenolic antioxidants, secondary aromatic amine antioxidants, sulfurized phenolic antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, organic sulfides, disulfides, and polysulfides. Other components can include seal swell compositions, such as isodecyl sulfolane (that is, isodecyl-3-sulfolanyl ether), which are designed to keep seals pliable. Also permissible are pour point depressants, such as alkylnaphthalenes, polymethacrylates, vinyl acetate/fumarate or /maleate copolymers, and styrene/maleate copolymers. All of the foregoing materials are well known and commercially available. They are described in greater detail in PCT publication WO00/70001.

[0044] The composition used in the present invention can be supplied as a fully formulated lubricant or functional fluid, or it can be supplied as a concentrate. In a concentrate, the relative amounts of the various components will generally be about the same as in the fully formulated composition, except that the amount of oil of lubricating viscosity will be decreased by an appropriate amount. The absolute percentage amounts of the remaining components will be correspondingly increased.

[0045] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

- (1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);
- (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
- (3) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the

context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbonyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbonyl group.

[0046] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

EXAMPLES

Examples 1 and 2

[0047] A first base formulation is prepared to which includes 83-86 percent of a 100N base stock, 5.8 percent of a polymethacrylate viscosity modifier, 4.5 percent dispersant(s), 1.0 percent overbased calcium sulfonate detergent, additional diluent oil, and antioxidants and other conventional components at lower levels, each containing the amounts of diluent oil conventionally present in that component. The formulation also contains 0.05% of an alkylated dimercaptiothiadiazole and 0.05% of tolyltriazole. To this first base formulation is added the phosphorus additives in the amounts shown in Table I.

[0048] The formulations are tested by the FZG pitting test. In this test a Strama™ FZG Gear Oil Test Rig and "C" profile gears 14 mm wide are used. After a break-in period, the test is run with a loading of 453 Nm (334 lb. ft.) on the wheel at 1440 r.p.m. and 90°C. The gears, lubricated with the 1.25 L of test fluid, are inspected and rated every 24 hours until failure or 300 hours, whichever first occurs. Failure is defined as 4% damage of a single tooth or 1% of the total load-carrying surface. In the results, higher numbers (number of hours) are preferred. The results are shown in Table I.

Table I

Example	1*	2
Additional components	amount (%)	
di-butyl phosphite	0.00	0.20
triphenylthiophosphate	0.04	0.00
85% phosphoric acid	0.03	0.03
di-phenyl phosphite	0.20	0.00
FZG Pitting Test, Hours	96	300

* A comparative example

The results show that pitting performance is particularly good when di-butyl phosphite is present in the formulation.

Examples 3-8

[0049] A second base formulation is prepared to which includes 83-86 percent of a 100N base stock, 6.3 percent of a polymethacrylate viscosity modifier, 3.1 percent dispersant(s), 1.8 percent overbased calcium sulfonate detergent, 0.2 percent dibutylphosphite, additional diluent oil, and antioxidants and other conventional components at low levels, each containing the amounts of diluent oil conventionally present in that component, including 0.05 percent of a zinc dialkyldithiophosphate. The formulation also contains an alkylated dimercaptiothiadiazole and/or a tolyltriazole in the amounts set forth in Table II.

[0050] Pitting performance of each composition is tested by the FZG micropitting Test Procedure KH HNR.192. This test uses the same setup as the above-described FZG Pitting Test, but examines performance at 1166 r.p.m., 265 Nm, and 120°C oil temperature. Each pinion tooth is examined microscopically and the extent of micropitting is recorded as a percent of total tooth area. The results, expressed as % Area after 41 hours test duration are reported in Table II. In this test lower numbers are preferred.

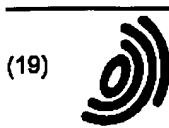
Table II

Example	3	4	5	6	Commercial Reference Material
Additive	amount (%)				
alkylated dimercapthiadiazole	0.032	0.05	0.32	0.0	—
tolyl triazole	0.0	0.05	0.0	0.05	—
Area, %	20.5	22.7	2.2	19.1	54.7

[0051] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. As used herein, the expression "consisting essentially of" permits the inclusion of substances which do not materially affect the basic and novel characteristics of the composition under consideration.

Claims

1. The use of at least one compound comprising a 5-membered ring containing at least two double bonded nitrogen atoms, to impart improved metal pitting performance to a fluid when said fluid is used in the lubrication of a transmission; wherein said fluid comprises an oil of lubricating viscosity, and wherein said fluid further comprises a hydrocarbyl ester of a phosphorous acid.
2. The use as in claim 1, wherein the compound is selected from aromatic triazoles and mercaptothiadiazoles.
3. The use as in claim 1 or claim 2 wherein the fluid comprises both an aromatic triazole and a mercaptothiadiazole.
4. The use as in claim 2 or claim 3 wherein the aromatic triazole comprises tolyl triazole and the mercaptothiadiazole comprises 2,5-bis-(tert-nonyldithio)-1,3,4-thiadiazole.
5. The use as in any preceding claim wherein the amount of the compound is 0.02 to 0.5 percent by weight.
6. The use as in any preceding claim wherein the fluid further comprises at least one succinimide dispersant.
7. The use as in claim 6 wherein the succinimide dispersant is a borated dispersant.
8. The use as in any preceding claim wherein the hydrocarbyl ester of a phosphorous acid comprises a dialkyl hydrogen phosphite.
9. The use as in any preceding claim wherein the fluid further comprises a phosphorus acid.
10. The use as in any preceding claim wherein said fluid further comprises 0 to 0.1 percent by weight of a zinc salt of a sulfur-containing phosphorus acid.
11. The use as in any preceding claim wherein the transmission is a continuously variable automatic transmission.
12. The use as in claim 11 wherein the continuously variable transmission is a belt drive transmission.



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 308 496 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
28.05.2003 Bulletin 2003/22

(43) Date of publication A2:
07.05.2003 Bulletin 2003/19

(21) Application number: **02257642.5**

(22) Date of filing: **05.11.2002**

(51) Int Cl.7: **C10M 141/10, C10M 167/00**
// (C10M141/10, 133:44,
135:36, 137:02),
(C10M167/00, 125:24, 133:44,
133:52, 133:56, 135:36, 137:02,
137:10, 145:14, 159:16,
159:24), C10N30:06,
C10N40:04

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **06.11.2001 US 332932**

(71) Applicant: **The Lubrizol Corporation**
(an Ohio corporation)
Wickliffe Ohio 44092-2298 (US)

(72) Inventors:
• **Sumiejeki, J.L.**
Mentor, Ohio 44060 (US)
• **Ward, William C.Jr.**
Perry, Ohio 44081 (US)

(74) Representative: **Crisp, David Norman et al**
D. YOUNG & CO.
21 New Fetter Lane
London EC4A 1DA (GB)

(54) **Transmission fluids exhibiting reduced pitting**

(57) Compounds comprising a 5-membered ring containing at least two double bonded nitrogen atoms can be used to impart improved metal pitting performance to a transmission fluid. The fluid includes an oil of lubricating viscosity and a hydrocarbyl ester of a phos-

phorous acid and is preferably limited to 0 to 0.1 percent by weight of zinc salts of sulfur-containing phosphorus acids.

EP 1 308 496 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 25 7642

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 976 813 A (CHEVRON CHEM SA) 2 February 2000 (2000-02-02) * page 2, line 10 - line 22; claim 9; examples 1-6 * * page 3, line 7 - line 18 *	1-12	C10M141/10 C10M167/00 //(C10M141/10, 133:44,135:36, 137:02), (C10M167/00, 125:24,133:44, 133:52,133:56, 135:36,137:02, 137:10,145:14, 159:16, 159:24), C10N30:06, C10N40:04
A	US 4 354 949 A (EGGERS CARL A ET AL) 19 October 1982 (1982-10-19) * column 1, line 5 - line 35 * * column 3, line 40 - line 50 *	1	
A	US 4 609 480 A (HATA HITOSHI ET AL) 2 September 1986 (1986-09-02) * column 1, line 9 - line 23; claim 1; table 1 * * column 3, line 4 - line 25 *	1,2,4	
A	US 5 759 965 A (SUMIEJSKI JAMES L) 2 June 1998 (1998-06-02) * column 26, line 37 - line 42; claim 1; tables I-III *	1-12	
A	EP 0 978 555 A (ETHYL CORP) 9 February 2000 (2000-02-09) * paragraph [0042]; claims 1-22 *	1-12	
A	EP 1 142 983 A (IDEMITSU KOSAN CO ;NSK LTD (JP)) 10 October 2001 (2001-10-10) * paragraphs [0001],[0038],[0042]; claims 1-13 *	1-12	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 3 April 2003	Examiner Glod, G
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 02 02 (P04001)

BEST AVAILABLE COPY

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 25 7642

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

03-04-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0976813	A	02-02-2000	EP 0976813 A1	02-02-2000
			JP 2000063870 A	29-02-2000
			SG 72973 A1	23-05-2000
US 4354949	A	19-10-1982	AU 545294 B2	11-07-1985
			AU 6653281 A	30-07-1981
			CA 1169847 A1	26-06-1984
			DE 3162912 D1	10-05-1984
			EP 0033170 A2	05-08-1981
			JP 1583895 C	22-10-1990
			JP 2009080 B	28-02-1990
			JP 56109293 A	29-08-1981
			PL 229332 A1	18-09-1981
			ZA 8100442 A	24-02-1982
US 4609480	A	02-09-1986	JP 1751383 C	08-04-1993
			JP 4032877 B	01-06-1992
			JP 60084394 A	13-05-1985
US 5759965	A	02-06-1998	CA 2189208 A1	17-01-1998
			JP 10168480 A	23-06-1998
			AU 717747 B2	30-03-2000
			AU 7023996 A	24-04-1997
			EP 0769546 A2	23-04-1997
EP 0978555	A	09-02-2000	US 6034040 A	07-03-2000
			AU 3583499 A	24-02-2000
			CN 1243863 A ,B	09-02-2000
			EP 0978555 A1	09-02-2000
			JP 2000063877 A	29-02-2000
EP 1142983	A	10-10-2001	US 6352962 B1	05-03-2002
			EP 1142983 A1	10-10-2001
			US 2002055441 A1	09-05-2002

EPO FORM P0189

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

BEST AVAILABLE COPY